Mediterranean Archaeology and Archaeometry, Vol. 6, No 2, pp. 77-91

The dating of ancient metals: review and a possible application of the ^{226}Ra/^{230}Th method (a tutorial)

Liritzis Ioannis

Laboratory of Archaeometry, Dept of Mediterranean Studies, University of the Aegean, 1 Demokratias Ave., Rhodes 85100, Greece (liritzis@rhodes.aegean.gr).

Received: 15/7/2006
Accepted: 12/11/2006

Abstract

Based on the known U-disequilibrium decay law whereof several dating methods have been devised (e.g. in dating speleothems, paintings, shells) a novel idea of dating ancient metals is presented based on the Radium-226 separation from metal during the smelting process. ^{226}Ra is gone with slag and its products, while in metal it grows from remaining traces of ^{238}U. Within about 8,000 years the growth reaches equilibrium which sets the upper limit to the method. A review of indirect dating methods of metallurgical remains is outlined, while the advantages and limitations of the novel method is discussed in connection to these metallurgical activities based on preliminary isotopic data.

Keywords: *uranium, isotopes, dating, metals, alpha counting, radioactive, Radium-226, ores, bronzes.*

Introduction

Early metallurgy starts with the exploitation of native copper and gold and copper ores (Piggot 1999; Hartmann & Sangmeister 1972; Tylecote 1987; Moorey 1994; Notton 1974). Native copper and gold were used before Early Bronze Age Europe, unalloyed with other metals, subjected initially to annealing –the first step toward true metallurgy- and next to consolidation by melting and simple casting of molten into molds, and often solely shaped by cold hammering and cutting of the cast piece. Later at some point copper ores were discovered and their smelting which lead to bronzes.

Copper metallurgy has started in different times amongst different cultures flourishing in the Mediterranean and Near East. Archaeological evidence suggests that copper was first used between 8,000- 5,000 B.C., most likely in eastern Anatolia to Mesopotamia and –toward the end of this period- the Indian subcontinent (Piggot 1999; Moorey 1994).

In Greece it appears during 5th millennium BC known as late Neolithic period and corresponds in the development of an 'indigenous metallurgy' in Balkans during Bronze Age (Renfrew 1967; McGeehan, 1996; Arfara, 2007).

These metals replaced lithic tools around 3rd millennium BC. Such 'invasion' was realized with the practice of pyrometallurgical technologies of ore melting. At the same time metals become abundant takes place greater development and extension of trade and like handmade artifact specialization, two factors that lied down the basis of the coming 'first embryonic cultures' (McGeehan 1983; Arfara 2007).

Archaeometrical research has been directed to the reconstruction of early trade routes and contacts of ancient but mainly prehistoric societies and their technological development, from the location of metallurgical sources (ore deposits) and analysis of metal artifacts through lead isotope and other physical methods of chemical analysis.

Metallurgical slags are very important materials to study since they are direct evidence of pyrometallurgical processes and can provide us with clues regarding way of metal acquisition – from the melting of native copper (or re-melting of different objects) and smelting of ore. This point has particular interest regarding the earliest attempts of metallurgical techniques in the 3rd millennium BC (Tylecotte 1970, 1987).

Slags offer important information about ancient technology and are datable by TL. The latter becomes even more useful when it is referred to early metallurgy (Liritzis and Liritzis 1986).

The dating of metallurgical processes is made indirectly by,

a) dating datable materials associated with these processes by thermoluminescence (TL) and Optical stimulated luminescence (OSL) of burnt soil in kilns and crucibles, of remaining core material in the metal artifact and slag products (Elitzsch et al. 1983; Lefferts et al. 1981).
b) radiocarbon (C-14) applied on carbon found in trapped slag inclusions and even through the carbon from the carbides in the smelting of ores using charcoal (mineral fuel) itself, using AMS C-14,
c) ageing processes of gold-copper-silver alloys i.e. phase separation and/or ordering, over the course of time (Seruya and Griffiths, 1995) - by determining the rates of these ageing processes which involve slow progress towards ambient temperature equilibrium, provide a 'clock' that can be used to develop a new approach to the dating of gold-copper-silver alloys, that provides some indication of its date of manufacture. Even a very rough indication of age might be valuable in many cases.[1]
d) the hitherto attribution of an age from their association with other archaeological artifacts, or on stylistic grounds, i.e. regarding the sculpture, its pose, iconography, base, with other words the typology and morphology (Reedy 1997).
e) Corrosion processes, the formed patina may differentiate between an old from a recent object. Corrosion is extremely variable depending on the particular conditions every metal item has been subjected (Lefferts et al. 1981).

It cannot be ruled out that the early melting was carried out in charcoal hollows in a larger scale version of present day simulation experiments (melting point for copper 1083° C and for gold 1063° C).

With native metal pieces of gold from alluvial sediments, repeated remelting changes the composition. In fact during melting of alluvial gold some solid debris is seen to float on the surface of the molten gold rather representing a combination mainly of gangue material from alluvial grains and ash traces. Subsequent analyses (SEM-EDXRF, LA-ICP-MS) have shown evidence of successive loss of certain elements, particularly lead and the higher bismuth as they are more volatile at the melting point of gold, and of strontium associated more with gangue material that join the surface detritus (Taylor et al., 1995). Most native gold artifacts contain associated major elements of silver (up to 30%) and copper (up to 20%), with trace elements to follow. It is this fact of differences in trace/ultratrace element composition that gold 'fingerprint' is based. It is this premise that gold associated with a specific mineralizing event can inherit a particular minute element signature unique to that event or process, and that this signature can be detected in early gold artifacts where they have been manufactured by the melting up and forming of the alluvial gold. It can however been assumed that there is a low probability of the mixing of gold from different sources during this early period of gold use. Then the signature may be modified by the relative loss of elements in the melting process, either by the evaporation of more volatile constituents, or preferential separation with the lighter gangue material in the melt. The process is significantly less severe in the modification of the composition of the metal gold as compared to the major partitioning of trace element that takes place during the chemical reduction in the smelting of a metal, such as copper, from a sulphide or carbonate ore. The trace composition can also be significantly modified in subsequent alloying.

Basic carbonates malachite (bright green, $CuCO_3$. $Cu(OH)_2$, specific gravity=4) and azurite (light blue, 2 $CuCO_3$. $Cu(OH)_2$, specific gravity=3.8,) have been exploited in oxidized zones of copper deposits (and rarely as a cemented material in sandstones), especially in areas where there is much supergene alteration, which created the friable nature (fracture is conchoidal and brittle) of the parent rock containing these ores. This allowed the Bronze Age miners to extract them using rib bones, picks of sharpened long bones with condyle still attached for ease of gripping, and hammers made from small beach boulders. Evidence from small 'chips' or fragments of bronze, suggest that metal implements may also have been used. Ore was separated by hand, and the malachite and azurite, both brightly coloured, were selected.

Study of ancient and prehistoric metallurgy at first involved analytical work on metal composition sought to distinguish quantitatively and semi-quantitetively between copper, copper alloys and tin-bronzes, differentiation between native and smelted copper and determination of whether and where sulphide, as opposed to oxide, ores were smelted (Balthazar, 1990; Knapp, 2000). However, provenance studies for metals, especially about copper trade in the Mediterranean Bronze Age, has attracted special attention, though multiple questions are still unanswered related to mixing and lead isotope fields overlapping effects (Muhly, 1989; Knapp, 2000).

The first use of metal is native copper and gold. Eventually, native copper sources were exhausted and copper oxides with striking colors those of malachite (green) and azurite (blue) were exploited.

The recognition and selection of metal ores, the knowledge of metal extraction and their hard properties by prehistoric people for making tools and weapons but also for religious and cosmetic use, must have a long cumulative experience of millennia in their endeavor to secure everyday needs of hunting and gathering purposes, cultivation and agricultural activities.

The metal finds vary from pins, bracelets, jewelry, spearheads, axes to coins and of variable size statues.

A dating method directly applied to metal artifacts is missing. Any such method obviously would help archaeological interpretation regarding earliest metal production, metal trade, and questions of authentication.

Along the latter notation we are presenting a first attempt to dating metal finds based on ^{226}Ra daughter isotope of the ^{238}U series (Liritzis, 1983b).

However, it is necessary to first briefly report on the metal (bronze) and slag composition and the isotopic fractionation during smelting, as well as the current U-disequilibrium dating methods of various materials, since the newly proposed method is based on such decays.

Metal and slag composition

Metal finds from archaeological contexts since prehistoric times are summarized into mainly bronzes, iron-based, lead and lead oxhides, gold and silver.

Composition (chemical elements and mineralogy) is revealed from chemical analysis and metallographic sections.

Bronzes for example consist of >90% copper alloyed with tin (Sn) or arsenic (As), lead (Pb) or antimony (Sb). The added elements range between 0.05 to 9%, the max values attributed to As, Pb, Sn for the Bronze Age (Renfrew, 1967; Craddock, 1976; Maddin & Muhly, 1974; Charles, 1967; Madin, 1987; Northover, 1987).

Copper extracted from smelting (Cu specific gravity= 8.93 g/cm^{-3}, melting point.= 1083° C, boiling point=2580° C), contain trace of arsenic and other contaminant elements derived from original ore remained from the smelting during ore reduction (Sn, Pb, Fe, Ni, Ag, Bi), all amounting to about 1%.

The evolution of mixing, separation and smelting techniques follow progressive phases. Thus, arsenic bronzes of Early Bronze Age, for example, follow tin bronzes during Middle Bronge Age, while lead is introduced during Mycenean period and establishes as an deliberate alloy during Geometric period. Progressively, the practice of alloying is introduced, accidental contamination is recognized and becomes conscientious the deliberate choice of raw material depending on use.

Depending on the type of ore ancient slags contain the major element oxides CaO, TiO_2, K_2O, Na_2O, Al_2O_3, MgO, SiO_2, MnO, Fe_2O_3 and trace elements (Papademetriou et al., 1988; Bachmann, 1988; Liritzis et al., 2007).

Ores contain traces of uranium, thorium and their daughter products derived from their radioactive decay. On average, uranium in copper ores is 2.4 ppm (1-3 ppm) and thorium-232 in ores is 0-1 ppm (1 ppm U-238= 2.53×10^{15} atoms per gram) (Liritzis, et al., 2007). Due to the high age of ores, uranium series is in secular equilibrium, i.e. the number of produced nuclei equals those that decay for the short and long-lived parents. However, during smelting of Cu ores some element oxides of high specific gravity (sp.g.>6 g/cm^3) in earliest trials were contaminants, and with later progress (early Bronze Age) were deliberate additions to metal copper. Such metal elements with high/medium specific gravities (in g/cm^3) and high-low melting points (° C) included: As (sp.g.=5.7, m.p.=817), Sn (sp.g.=7.3, m.p.=232), Pb (sp.g.=11.3, m.p.327), Sb (sp.g.=6.7, m.p.=630), Ni (sp.g.=8.9, m.p.=1453), Ag (sp.g.=10.5, m.p.=961). Uranium and thorium isotopes with their high specific gravity are withdrawn into the metal phase, while radium with the sluggish phase of smelting.

Isotopic separation / fractionation

The separation / fractionation of U and Th daughter products during smelting lacks in literature, but the process broadly resembles melting in magma chambers (Tarbuck and Lutgens 1987). There are quite a number of mechanisms in operation in a smelting furnace (more like a magma chamber). At least four of them are, a) sorting by density, b) sorting by melting point, c) sorting by how easily something is incorporated into minerals that form at the slag product (like the top of a magma chamber) (sometimes one has repeated melting and solidification, introducing more complications), and d) differences in solubilities (Faure 1986). Surely, it is hard to keep track of this all, much alike especially with the difficulties encountered in exploring magma chambers. However, the main difference with magmas is the lower melting point ores are subjected, since by the 1100° C the melting point of of Cu, Ag and Au is reached. Thus, these mechanisms will be definite factors that may change relative concentrations of parent and daughter isotopes in some way in magma processes but not effective in smelting processes.

Thus, most lavas have excess radium today. High Ra-226/U-238 ratios are a common feature of primitive magmas, which magma-generating processes produce. Radium-226 has a low melting point (700° C = 973 degrees K) which may account for its concentration at the top of magma chambers i.e. the sluggish products poured away the metal phase deposited in the bottom.

A very interesting anomaly is reported regarding the ^{238}U decay chain, which is ^{238}U, ^{234}U, ^{230}Th, ^{226}Ra, ^{222}Rn, ^{218}Po, ^{214}Po, ^{210}Po, ^{210}Pb, ^{210}Bi, ^{206}Pb (Cortini, 1982). The half life of ^{238}U is 4.47×10^9 years and that of ^{226}Ra is 1.6×10^3 years. Thus radium is decaying 3 million times as fast as ^{238}U. At equilibrium, which should be attained in 500,000 years for this decay series, we should expect to have 3 million times as much ^{238}U as radium to equalize the amount of daughter produced.

Geologists discovered that ten times more ^{226}Ra than the equilibrium value was present in rocks from Vesuvius. They found similar excess radium at Mount St. Helens, Vulcanello, and Lipari and other volcanic sites. The only place where radioactive equilibrium of the ^{238}U series exists in zero age lavas is in Hawiian rocks. Thus instead of having 1/(3 million) as much radium as uranium, which we should expect, there is ten times as much, or 1/(300,000) times as much radium as uranium (Cortini 1982).

How is this excess of radium being produced? This radium cannot be the result of decay of uranium, since there is far too much of it. Either it is the result of an unknown decay process, or it is the result of fractionation which is greatly increasing the concentration of radium or greatly decreasing the concentration of uranium. Thus only a small fraction of the radium present in the lava (at most 10 percent) is the result of decay of the uranium in the lava.

U-Series disequilibrium dating methods

Disequilibrium occurs if the U-series "closed system" is disturbed, either by dissolution of radiochemical agents (leaching/ enrichment) or firing at melting temperatures.

In fact the decay scheme of U-238 is: ^{238}U($t_{1/2}$=4.47E9 years)- ^{234}Th(24.1 days) ^{234}Pa(1.17 min)-^{234}U(2.45E5 yrs)-^{230}Th(75.4E3 yrs)-^{226}Ra(1600 yrs)-^{222}Rn (3.83 days)-^{218}Po (3.05 min)-^{214}Pb (26.8 min)-^{214}Bi (19.9 min)-^{214}Po (162 μs)-^{210}Pb (22.2 yrs)- ^{210}Bi (5.01 days)-^{210}Po(138.4 days)-^{206}Pb (stable) (Lorenz, 1983; Liritzis & Kokkoris, 1992).

Activity is defined as = $dN/dt = -\lambda.N_t$, from which the radioactive decay law derives

$$N_t = N_0 e^{-\lambda t} \qquad (1)$$

Where N_0 is the number of active atoms present at the beginning of the observations (t=0) and λ is the radioactive decay constant. The mean life is defined as

$$\tau = 1/\lambda \qquad (2)$$

For the half-life $t_{1/2}$ during which half the atoms disappear by decay is given by:

$N_0/2 = N_0^{e-\lambda t_{1/2}}$ from which,

$$t_{1/2} = \log e2/\lambda = 0.693.\tau = 0.693/\lambda \qquad (3)$$

The activity ratios U-234/U-238 andTh-230/Th-232, Ra-226/Th-230, Th-230/U-234 vary in nature depending on the type of the involved rock. Rocks unaffected by weathering for 1 million years the ^{238}U-^{234}U- ^{230}Th are in secular equilibrium. Exposure to weathering forces may imitate processes causing disequilibrium. In the course of weathering and erosion chemical and biochemical agencies dynamically influence the distribution patterns of uranium and thorium, as well as all the nuclides produced by radioactive decay of these elements. Radioactive degradations of the rock-borne ^{238}U, ^{235}U and ^{232}Th nuclides create many additional nuclides, which are distributed among many different chemical elements. Chemical reactivity of these elements fluctuates between radon, a noble gas, and the tetravalent Th4+, which is absorbed and held tenaciously on particle surfaces. The U-234/U-238 ratios in various soil types and rocks vary between 0.80 to 1.20 (Liritzis 1989b; Hansen and Stout 1968). Moreover the groundwater percolation has noticeable effect on the transport of sediments through fissures in the rocks as a result of weathering / erosion processes. Such sediments therefore must partially reflect isotopic ratios of the groundwater action. In Finland, analyses of groundwater from bedrocks gave U-234/ U-238 ratios ranged from 0.76-4.67 and U-238/Ra-226 ratios that ranged from 1 to 20. The high U-238 /Ra-226 activity ratios were found particularly in samples with an elevated U-content and may have resulted rather from the selective leaching of U than from the lack of Ra-226 in the formation involved (Asikainen 1981).

This disequilibrium effect has been used elsewhere as the basis of dating: a) white lead (Pb-210) pigment dating (Keisch1970; Keisch et al. 1967), and b) U-Th of speleothems (stalagmites, stalactites, travertines, flowstones) (Liritzis 1982, 1989a; Liritzis and Galloway 1982b; Schwarcz 1980; Ivanovich et al., 1992).

An appreciation of the disequilibria effect is gained from the family of built-up curves of dose temporal variation derived from U-series for various conditions of parent ^{238}U to daughter isotopes ^{234}U, ^{230}Th and ^{226}Ra, based on the U-238 decay scheme (see, fig.1 in

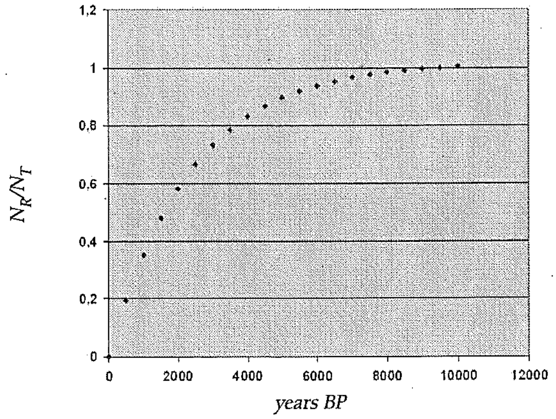

Figure 1a. Growth curve of Ra/Th activities (eq.9 in text) for $N_R(0)$= 0. Equilibrium between Ra-226 and Th-230 is achieved at around 10.000 years.

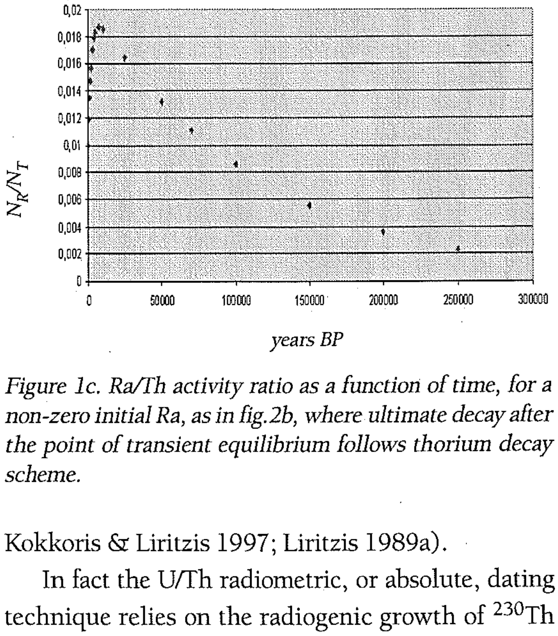

Figure 1c. Ra/Th activity ratio as a function of time, for a non-zero initial Ra, as in fig.2b, where ultimate decay after the point of transient equilibrium follows thorium decay scheme.

Kokkoris & Liritzis 1997; Liritzis 1989a).

In fact the U/Th radiometric, or absolute, dating technique relies on the radiogenic growth of ^{230}Th back to 'secular' equilibrium with its parent ^{234}U and ^{238}U isotopes. If the initial value of ^{230}Th is zero (as is usually the case in speleothems) then it takes about 350,000 yrs (as measured by alpha-spectrometry) or 500,000 yrs (if measured mass-spectrometrically) to re-establish equilibrium. So the U-series dating method is useful up to that limit and it usefully complements and extends the radiocarbon method in many cases. The dating of stalagmites, hot-spring deposits and fossil corals is relatively straightforward unless contaminated by dirt. In such cases various lab techniques are developed to deal with the problem. The U-Th method has found good use in dating archaeological cave sites and hominid sites (Liritzis 1980 a, b; 1983; Liritzis & Galloway 1982a; Schwarcz and Latham 1989; Ivanovich et al. 1992).

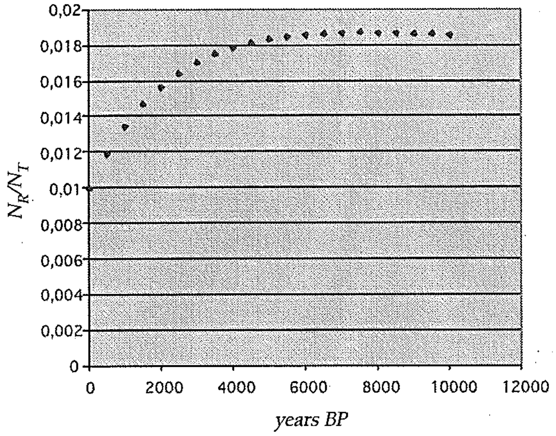

Figure 1b. Radium growth for a non-zero $N_R(0)$ (=0.1 dpm) which depends on the amount of activity initially present. The greater $N_R(0)$ pulls transient equilibrium peak to younger ages ($N_T(0)$=10).

In Pb-210 dating this method is based in the radioactive decay of lead isotope Pb-210, in a similar way to C-14 decay. The white lead pigment is produced from the extraction of metallic element Pb-210 from the smelting of sulfuric ore PbS which process results to production of galena or litharge (PbO + Ag + other contaminants). Within this ore uranium traces with daughter products in equilibrium exist. Such radioactive equilibrium is destroyed by the high temperature during smelting in kilns and their casting in molds. Lead ore is processed to form white lead with a result radium is removed with other waste products (slag (litharge) products), while lead ^{210}Pb remains with the metal (specific gravity of Pb= 11.34 g/cm^3).

Thereafter ^{210}Pb decays exponentially with a half-life of about 22 years without any more supported by parent ^{226}Ra, an alpha particles emitter. However, secular equilibrium is reached within about 200 years due to traces of ^{226}Ra remaining in the white powder.

Such drastic drop in radium concentration from smelting can amount to 0.1 decays per min / gm of Pb (units of dpm/g, disintegrations per minute per gram).

TABLE 1

Some 'classical' constant of Radium-226

Constants	**Value**
Half-life ($t_{1/2}$)	1622 years
Decay constant, λ	4.3322 E-04 yr^{-1}
Number of α-particles emitted per second from 1 g of Ra	3.60810E10
Number of α-particles emitted per second from 1 Curie of Ra	3.701E10
Heat emitted per hour by 1 g of radium in equilibrium with its products	619 Joule
Specific gravity	5-6 g/ cm^3
Density	5 g/cm^3
Melting point	700° C
Boiling point	1140° C

Appendix

Thorium has density = 11.5 g/cm^3, melting point 1,700° C and boiling point 4,200° C. On the other hand Uranium has density = 19.05 g/cm^3, melting point 1,133° C, and boiling point 3,800° C. The relation between mass and activity is $m = A^*(AW)/ \lambda^* N_A$, A=activity, AW atomic weight, λ decay constant of isotope = $0.69/t_{1/2}$, and N_A Avogadro's number= 6.023^*10^{23} atoms/mole, and Specific activity = $n / 0.693^* t_{1/2}$ dpm/g or Bq/g, where n = number of nuclides /g = Avogadro number (atoms/mole) / (g/mole) nuclide.(e.g. $\lambda_{Pb} = 0.031$ /yr). From the above, the relation between activity and content is: 1 Bq = 1 disintegration / sec = 27 pCi, and 1 Ci = 3.7E10 decays / sec (= Becquerel) or 1 pCi= 1.16E6 decays/ yr. Then, 1 ppm ^{238}U = 2.35E15 atoms U-238/g and 1 pCi /g ^{238}U = 3.03 ppm, 1 pCi /g ^{232}Th = 9.15 ppm and 1 pCi/g ^{226}Ra= 10E-6 ppm, and 1 pCi/g ^{230}Th= 0.048E-3 ppm. For parts of the decay chain the absorbed dose is: ^{226}Ra-^{206} Pb = 29.27 MeV alphas, so 1.166E6 pCi/g *29.27 MeV/yr = $34^*106^*1.6^*10^{-7}$ = 5.46 mGy/yr. The relationship between activity and absorbed dose rate is: 1 Bq/Kg ^{238}U = 0.0116 mGy/yr, 1 Bq/kg ^{232}Th = 0.00702 mGy/yr. 1Bq/Kg ^{226}Ra = 2.74E-8 ppm, and 1 Bq/Kg ^{210}Pb =3.53E-10 ppm.

This tiny activity may start as 10 milligrams of sample will eventually approach background level of noise, something about 0.001 dpm/g i.e. 100 times smaller activity.

The ^{210}Pb activity in a recent painting may be between 1 to 150 dpm/g which depends on original ore deposit.

A low activity soon decays away and detection becomes extremely difficult and the dating impossible.

The dating method is given by eq (4)

$$Pb_t - Ra_t = (Pb_o - Ra_t)\exp(-\lambda.t) \qquad (4)$$

Where Pb_t and Ra_t are measured activities, Pb_o initial activity, $\lambda = 0.031$ disintegrations per year, and t the time elapsed since separation of isotopes.

Without knowing initial Pb, dating is impossible. However this equation aids authenticity tests, since modern day paintings is expected to contain unequal amounts of Ra-226 and Pb-210. A noticeable example for this dating method concerns a forged painting, the Disciples of Emmaus by Van Meegeren; the portrait was declared genuine by a noted art scholar and sold for $170,000.

In dealing with U-disequilibrium decay curves, the ^{236}Ra decay and ores' natural concentrations, as well as some characteristic constants of Radium-226 are given in Table 1, while the attached Appendix to the Table 1 provides useful conversion of units relating number of atoms, dose-rate, half-life and activity.

Along similar principles a dating method of metals has been devised based on the ^{226}Ra/^{230}Th disequilibrium ratio during smelting (Liritzis, 1983b).

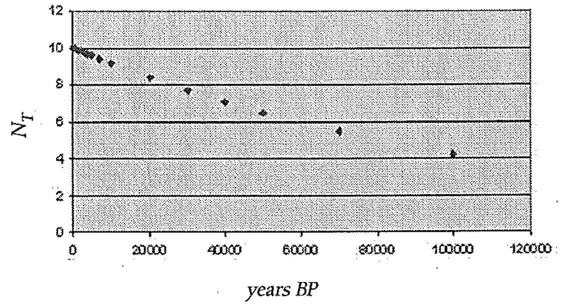

Figure 2. Thorium-230 decay scheme.

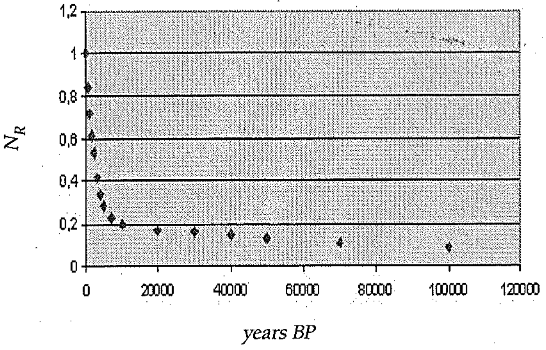

Figure 3. Sole Radium-226 decay without any thorium parent support.

The rationale of the radium dating of metals: a tutorial

During melting and smelting procedures of ores in kilns or open air fires (crucibles) and separation of slag from metal phase the radioisotopes are fractionated too. This is due to respective reactivity of these natural isotopes. Radium is an alkaline-earth metal, highly reactive and oxidizes in air, with valence states 0 and 2+. Oxidation potential is as great as those of Ca, Sr, Ba. Thorium with a valence 4+ is a member of actinide series and resembles to Zr and Hf. With halogens and organic acids forms common salts, and is tenaciously adherent to aluminosilicates. In contrast, Uranium is easily mobilized by hydrolysates.

Apart of the chemical reactivity, in particular, the ^{226}Ra daughter product of the ^{238}U series is withdrawn by slag products away of the melted metal, as a result of its lower specific gravity, ε= 5-6 g/cm^3 , and its lower melting point (700° C) than that of copper (1083° C). Thus disequilibrium is set with a zero expected theoretical ratio ^{226}Ra/^{230}Th in the metal.

Although the effect of U-series disequilibrium is significant for great ages compared to the half-lives of the involved isotopes and applies to palaeolithic times, the 1600 years half-life of ^{226}Ra is comparable to the elapsed time since the onset of metallurgy in prehistoric archaeology. Therefore ^{226}Ra production towards equilibrium with ^{230}Th follows the known exponential decay law of radioactivity for a time period equivalent to several half-lives which cover the whole of prehistory of the world (about 10,000 to 3,000 years before present). Therefore this growth of ^{226}Ra back to 'secular' equilibrium with its parent ^{230}Th is the basis of the new method. (Fig. 2a, Fig.4).

Disequilibrium between ^{238}U and ^{226}Ra is common with ^{226}Ra usually in excess. Once metal is separated from slag and its products, ideally radium (^{226}Ra) is gone with slag and metal remains free of radium.

Although this is accord with theory in practice traces may remain. Thereafter in metal ^{226}Ra is grown from ^{230}Th while ^{230}Th decays. Fig.1a shows the growth curve of eq.9 below, for $N_R(0)$= 0. Equilibrium is achieved at around 10.000 years. For a non-zero $N_R(0)$ the radium growth depends on the amount of activity initially present. The greater $N_R(0)$ pulls transient equilibrium peak to younger ages (Fig. 1b), thereafter ultimate decay follows thorium decay scheme (Fig.1c, Fig.2). The equations governing the process are:

For the decay of Th-230: $dN_T/dt = -\lambda_T N_T$ (5)

For the growth and decay of Ra-226:
$dN_R/dt = \lambda_T N_T - \lambda_R N_R$ (6)

Where N_T and N_R are the number of atoms of ^{230}Th and ^{226}Ra present at time t, and λ_T =8.664301 E-06 yr^{-1}.

Eq (6) may be solved to give N_T and N_R if the quantities or activity or disintegration rate, of these two atoms present at time t = 0 i.e $N_T(0)$ and $N_R(0)$, are known.

Thus, from eq.(5) and eq.(6):

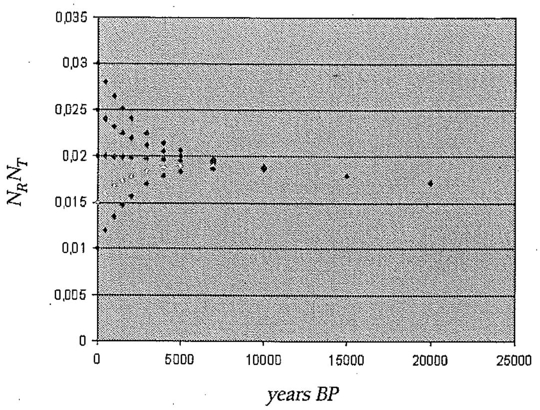

Figure 4a. Variation of N_R/N_T versus time of eq.(8) in the text, for $N_R(0) = 0.1$ (lower), 0.15, 0.2, 0.25, 0.30 (upper) dpm/g and $N_T(0)= 10$ dpm/g.

$$\text{Activity of Th} = \lambda_T N_T = \lambda_T N_T(0) e^{-\lambda_T t} \qquad (7)$$

$$\text{Activity of Ra} = \lambda_R . N_R = \lambda_R . N_R(0)\ e^{-\lambda_R . t} + \lambda_T \lambda_R\ N_T(0)\ [e^{-\lambda_T . t} - e^{-\lambda_R t}]/(\lambda_R - \lambda_T) \qquad (8)$$

Where λ_R, λ_T (=8.664301 E-06 yr^{-1}) decay constants of ^{226}Ra and ^{230}Th respectively (Kokkoris and Liritzis 1997; Liritzis and Kokkoris 1992).

It is assumed that initially in the deposited metal ^{226}Ra is not present, $N_R(0) = 0$, and then at any time

$$\text{Activity of Ra / Activity of Th} = \lambda_R[1 - e^{-(\lambda_R - \lambda_T)t}] / (\lambda_R - \lambda_T) \qquad (9)$$

For $\lambda_{daughter} > \lambda_{parent}$ (daughter shorter lived than parent), the activity ratio of eq. (9) increases with time and tends to the constant value $\lambda_R/(\lambda_R - \lambda_T)$, and both activities decay ultimately with the half-life of thorium-230. When this ratio has been established, a state of transient equilibrium exists. Thereafter, decay ratio is driven by thorium decay (Fig.1c and Fig.2).

The product activity reaches a maximum at a time given by $dN_R/dt = 0$, or from eq.(8) with $N_R(0)= 0$

$$\lambda_T e^{-\lambda_T t} = \lambda_R e^{-\lambda_R t} \qquad (10)$$

and the parent and daughter activities are then instantaneously equal. And at this time only the next equation exists (Fig.1c),

$$\lambda_R N_R = \lambda_T N_T \qquad (11)$$

If $\lambda_{daughter} >> \lambda_{parent}$ which is the case here (λ_R=4.33E-04 >> λ_T=8.66E-06) then the ratio of activities tends to unity i.e. the value $\lambda_R/(\lambda_R - \lambda_T)$, and we have the case of secular equilibrium in which daughter Ra isotope grows at a rate determined by its own decay constant until it reaches an activity equal to that of its parent Th (similarly the growth of radon from radium). Thereafter the decay is governed by parent thorium's rate. ^{230}Th decays as a function of time, but its $t_{1/2}$ is so long in comparison to the archaeological time in question that safely during this time span we regard the decay as linear (Fig. 1c and Fig.2).

In the case of long-lived parents, such as uranium or thorium, it is clear that when secular equilibrium has been established the quantities of successive products present are given by the equations:

$$\lambda_T N_T(0) = \lambda_R N_R = \lambda_{Rn} N_{Rn} \cdot \ldots = \text{constant} \qquad (12)$$

corresponding to ^{230}Th, ^{226}Ra and ^{222}Rn in the U-238 series (the stable end product of 206Pb is excluded from this constancy since it continually accumulates). The activities are constant throughout and the relative amounts of different products are inversely proportional to their decay constants. All above formulae have been elaborated by Bateman (Burcham,1973).

From measured activities of ^{226}Ra and ^{230}Th in metals eq.(9) is the age equation.

However, if traces of ^{226}Ra are present initially in the metal as $N_R(0)$ then eq.(8) is the age equation (Fig.1b). In the latter case one needs to know $N_T(0)$, and the initial trace amount of $N_R(0)$. ($N_T(0)$ and $N_R(0)$ in metals can be estimated from present day simulation experiments). Due to relatively high half-life of ^{230}Th (72,000 years) with respect to the archaeological period concerned (around 8,000 years), present day measured $N_T(t)N_T(0)$ for the 5-6,000 years time span. But still $N_R(0)$ remains unknown and only further experimental work may resolve the issue (Fig.3). However, if most ^{230}Th with its high specific gravity has gone into metal phase the remaining amount in slag will support the decayed ^{226}Ra in a

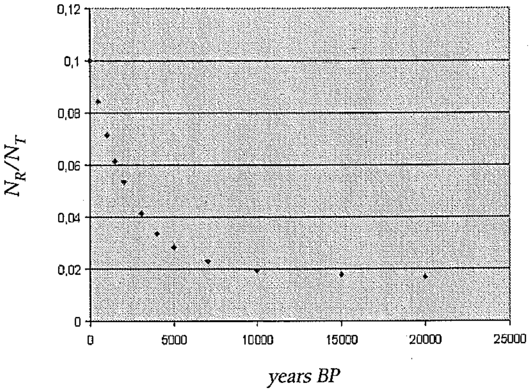

Figure 4b. for $N_R(0) = 1$, $N_T(0)=10$

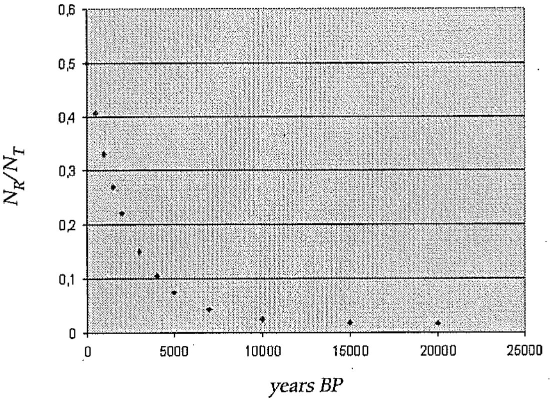

Figure 4c. for $N_R(0) = 5$ and $N_T(0) = 10$.

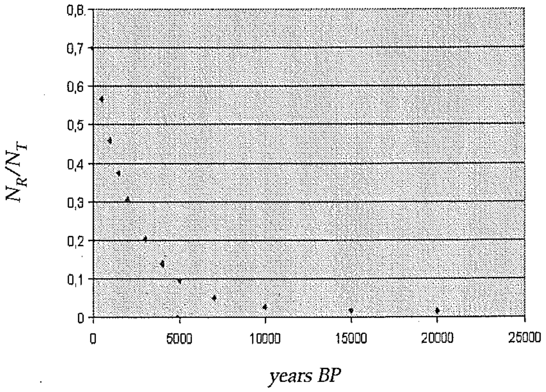

Figure 4d. for $N_R(0) = 7$ and $N_T(0) = 10$.

way similar to Fig.4 (a, b, c).

In any case, calculations of eq.(8) show that for low initial residual ^{226}Ra (e.g. 0.1 dpm/g) content in metal and low Ra/Th ratios << 0.02 the curve of N_R / N_T versus time exhibits a growth mode based mainly on ^{226}Ra which provides a near flat curve in the first 10,000 years. For higher ^{226}Ra content and Ra/Th ratios >> 0.02, the N_R / N_T versus time exhibits a decay mode based mainly on the ^{226}Ra decay which dominates ^{230}Th transformation to Ra (Figs.4). For example, for $N_R(0) \geq 1$ dpm and $N_T(0)=10$ dpm the decay mode that dominates is that of ^{226}Ra where the drastic variation within the 10,000 years is quite usable for age differentiation purposes. Again, here, as mentioned above, present ^{230}Th can be assumed equal to initial ^{230}Th. In fact within 10,000 this change reaches only a 10%, and up to 6,000 years this amounts to less than 5%. Thus, whatever amounts of it participates in the metal or slag phase it remains almost the same today. Thus, initial ^{230}Th can be safely assumed known and for $N_R(0) = 0$ or near zero the family curves of Fig.1c and Fig.4 for age determination may be used accordingly.

Measurements of ^{226}Ra in different ores from USA sites produced a wide range of values 0.18 – 140 disintegrations per gram of white lead (Braum, 1975).

Measurement of ^{226}Ra and ^{230}Th can be achieved by using refined radiochemical and mass spectrometric techniques, such as the traditional alpha spectrometry using ion exchange columns for isotopic separation and counting, thermal ionization mass spectrometry (TIMS), Multiple collector MC-ICP-MS, LA-qICP-MS and SHRIMP-SIMS. Mass quantity is restricted to milligram range and counting errors to 1-2%.With a detection limit of 0.0028 counts/min in alpha spectrometry the useful dating range is 2000 to 7000 years B.C. corresponding to errors of ±25 to ±2% respectively. Another technique to measure them is by alpha scintillation counting pairs technique with thick source (TSAC) but with a larger sample (Huntley et al. 1981, 1986; Aitken 1985; Liritzis and Galloway 1982) and TSAC with silicon pin detector (Michael & Zacharias, 2000). In the latter work continuous spectrum of alpha particles emitted from U and Th series is stripped in that the end point energies of the isotopes of interest are integrated and from devised equations regarding alpha particle ranges these isotopes are defined with accuracy depending from available material and radioactivity content. This is more or less similar to beta spectrum (Kurie plot), from plastic scintillator, stripping for determinationnof K, Th and U contents (see, Galloway and Liritzis, 1991). However, further work should be focused on radium fractionation and homogeneity issues and investigation of remaining traces in metals.

For finds made of native copper, where no smelting has taken place, the method is not applicable. However, the mixing of copper ores does not affect the method.

When metal finds re-melt to make a new metal artifact, the equilibrium is disturbed because radon and polonium are removed, though soon after some days equilibrium is set again. But the ^{226}Ra and ^{230}Th activities and their activity ratio is not affected by the secondary re-melting process. In this case the age refers to the metal finds made during first smelting and not to the later re-melting from mixing.

The accuracy of the method depends from the amount of sample and presence of isotopic measurements of ^{226}Ra and ^{230}Th being about 1-2%. However, for any residual minute traces of ^{226}Ra in the metal, it will be added to the radiogenically produced ^{226}Ra. The presence of $N_R(0)$ is not known but may vary from the efficiency of metal separation techniques.

Therefore, simulation experiments of smelting provide a clue regarding the quantities of these isotopes present. One would anticipate from modern day experiments ^{226}Ra in secular equilibrium with parent thorium-230 or uranium-238 in slag, and negligible in respective metal phase, a similar outcome occurring at the moment of ancient smelting. Thereafter supported ^{226}Ra from parent ^{230}Th grows towards equilibrium with U-series which is achieved within around 9,000 years, and unsupported Ra decays with its own half-life. Therefore, today measured U and Th from prehistoric slags by alpha counting (TSAC, thick source alpha counting employing the pairs technique; Liritzis & Galloway 1982b; Aitken 1985, 1990; Sjostrand and Prescott 2002) would be expected to provide similar to ore values for U and Th.

First experimental data and discussion

The alpha counter

Low-level alpha counter No. 7286 of Littlemore Scientific Instruments, Oxford, using ZnS (Ag) detector and with the built in software was employed applying the pair's technique to measure uranium and thorium contents (Aitken 1985; Sjostrand and Prescott 2002). The slow pairs determine the concentration of Th and the fast pairs the concentration of U. The calibration factors calculated for the estimation of Th and U, were made using the measured concentration of 15 standard samples (including clay, soil, granite, sandstones, limestones) (Liritzis et al. 2006)

U-calibration factor was 15.68±0.73 alpha pairs counts/ppm and the Th-calibration factor was 3.95±0.16 counts / ppm for all types. U and Th contents were alternatively calculated from analytical equations (Aitken 1985). No assumptions had to be made for the Th/U ratio.

First Application

Alpha counting using pairs technique was used on: a) ancient slag, b) modern slag, c) associated metal remain (prill), and d) contemporary finds of pure Al, Fe, Cu.

The ELSEC low level alpha counter with ZnS (Ag) screens was used. Slag were ground down to a mill to less than 90 micron, dried overnight at 80° C, sealed for one week and measured.

A) *The prehistoric slag of 3rd millennium B.C. from Abessalos site in Seriphos island (Aegean sea, Greece).* It gave 1.30±0.07 ppm for U and 0.80±0.17 ppm for Th, and no disequilibrium between ^{226}Ra and ^{224}U with errors involved of around 20%. The XRF analysis verified its silicious nature with major element concentrations, Si=39%, Fe=33.6%, Ca=11.7%, Cu=0.97%, Al=1%.

Various copper ore and copper oxide deposits measured by alpha counting pairs technique gave quite low natural Th and U values between zero to 2.5 ppm (Liritzis, et al., 2007).

B) *Slag and associated metal phase of copper prill from a simulated experiment.* These were extracted from last year simulation outdoors experiment (at "Demokritos" Research Center, Athens, by Dr Y.Bassiakos who executed the experiment and kindly provided the samples and chemical analysis), using a home made furnace bottom slag model, similar to that found in Crysokaminos, Crete. The ore was in pieces of almond like crop of cuprite and some malachite and the flux was quartz and calcite. XRF indicated the silicious nature of the obtained slag with major element content of Al=17.6%, Si= 38.5%, Fe=14.6%, Ca=5.3% and Cu=0.88%.

Measurements were performed using thick source alpha scintillation counting pairs technique. Uranium and thorium values of slag were 3±0.5 ppm and 4.9±0.6 ppm respectively. Results for slag indicated ^{226}Ra in equilibrium with the ^{234}U by the TSAC with silicon detector (TSAC) with errors around 20% (Michael & Zacharias, 2000; Liritzis & Galloway, 1982b). Measurements of a tiny copper prill by LA-QICP-MS gave Pb-210=0.0326 Bq/g (made for me at Tubigen by Dr E. Pernicka). In recent painting with white lead pigment Pb-210 ranges from 0.001-1.5 Bq/g. More spectrometry work is needed with a variety of metallic amounts and U concentrations to evaluate errors. Alternatively, the TSAC technique would be possible to measure the disequilibrium in metal finds following Huntley et al., (1986) provided that the sample is of some grams, has enough U content (a few ppm) and of circular shape to be accommodated into the sample holder. In very small sized samples only the mass spectrometry techniques can be used.

C) Accordingly, ^{226}Ra / ^{234}U disequilibrium - ^{226}Ra deficiency (absence) and ^{234}U presence- with associated errors around 20% was found for contemporary metal finds of aluminium, cupper and iron by TSAC, where U were in the range of 0.5-0.8 ppm and Th around zero (kindly provided by Dr C.Michael and Dr N. Zacharias at our request), reinforcing the validity of the new dating method.

Work in progress using Laser Ablation-Quadrupole ICP- Mass Spectrometry focuses on isotopic measurements of ancient slags and metals and contemporary simulation experiments.

Conclusion

This preliminary work reviews earliest metallurgical processes, outlines current dating approaches to metals and slags and indicates the potential of a new dating method of ancient metals. The smelting procedure removes radium and sets U-series in disequilibrium. Thereafter it grows from initially minute to zero activities towards equilibrium with direct parent thorium-230. Initial experimental data support this novel rationale, although much more work is needed to establish the validity of the method. The growth/decay curve of radium, due to its half-life of 1600 years, falls exactly within the archaeological period of interest. That is, from the earliest contact with ores, native metal and first trials of smelting in crucibles, during Neolithic period, through full production in Bronze Age, the Iron Age the Classical period to Medieval times makes a time span of around 7,000 years. The uncertainties can be defined and reduced through more spectrometric measurements of ancient and simulation smelting experiments. The method has a great potential and it is useful to dating especially prehistoric metallurgical activities and in authenticity tests.

Acknowledgements

I thank I. Arfara for making the measurements, Dr R. B. Galloway (Edinburgh) for useful comments, Dr Y. Bassiakos for providing the sample, and Dr C. Michael and Dr N. Zacharias for making some alpha counting with silicon pin measurements at NRC Demokritos.

References

Aitken.M.J (1985) *Thermoluminescence dating.* Academic

Press, London.

Aitken.M.J (1990) Pairs precision required in alpha counting. *Ancient TL*, 8, 12-14.

Arfara,I (2007) First contact of the Aegean cultures with metals (analysis and dating). Ph.D thesis, Dept. of Mediterranean Studies, Lab of Archaeometry, University of the Aegean, Rhodes, Greece (forthcoming)

Asikainen, M. (1981) Natural radioactivity of ground water and drinking water in Finland. *Institute of Radiation Protection*, STL-A39, p.65, Helsinki.

Bachmann, H.G (1988) *Scientific studies in early mining and extractive metallurgy.* British Museum.

Balthazar, J.W (1990) Copper and Bronze working in early through middle Bronze Age Cyprus. *Studies in Mediterranean Archaeology and Literature*, Pocketbook 84, Goteborg; P.Astrom's Forlag.

Burcham, W.E (1973) *Nuclear physics*, An introduction, 2nd edition, Longman, London.

Braum, M (1975) In *Applied Mathematical Sciences*, vol.15, Springer-Verlag, New York.

Charles, J. A (1967) Early arsenical bronzes- a metallurgical view. *Amer. J. Archaeology*, 71, 21-26.

Cortini, M (1982) *J. Vol. Geotherm Res.*, 14, 247-260.

Craddock, P. T (1976) The composition of the copper alloys used by the Greek, Etruscan and Roman civilizations. 1, *J. Arch. Sci.*, 93-113.

Elitzsch, C, Pernicka, E and Wagner, G.A (1983) TL dating of archaeometallurgical slags. *PACT* 9, II, 271-286.

Faure, G (1986) Principles of isotopic geology. John Wiley & Sons, New York, 589 p.

Galloway, R. B and Liritzis, I (1991) Scattering correction in beta dosimetry by beta particle counting. *Nuclear Tracks & Radiat. Meas.*, 18,1/2, 239-247.

Hansen. R. O and Stout. P. R, (1968) Isotopic distributions of U and Th in soils. *Soil Science*, 105, 1, 44-50.

Hartmann, A and Sangmeister, E (1972) The study of prehistoric metallurgy. *Angewandte Chemie International Editions in English*, Vol.11, Issue 7, 620-629.

Huntley, D. J and Wintle.A (1981) The use of alpha scintillation counting for measuring Th-230 and Pa-231 contents of ocean sediments. *Can. J. Earth Sciences*, 18, 419-432.

Huntley. D. J, Nissen.M.K, Thomson.J and Calvert.S.E (1986) An improved alpha scintillation counting method for determination of Th, U, Ra-226, Th-230 excess and Pa-231 excess in marine sediments. *Can. J. Earth Sciences*, 23, 959-966.

Ivanovich.M, Latham.A.G, and Ku.T-L, (1982) Uranium-series disequilibria applications in geochronology. Ch.3 In *Uranium series disequilibrium; applications to earth, marine and environmental sciences*, eds. Ivanovich.M and Harmon.R, Oxford U.P., 910 pp

Kokkoris, M and Liritzis,I (1997) Dose vesus time for U-disequilibrium and revised dose-rate data for TL/ESR dating. PACT 45, IV.5, 281-294.

Keisch, B (1970) In *Applications of science in examination of works of art*, 193 W.J.Young, ed, Museum of Fine Art, Boston;

Keisch. B, Feller.R.L, Levme. A. S, Edwards. R. R. (1967) Dating and authenticity of works of art by measurement of natural alpha emitters. *Science* 155, 1238-1242.

Knapp. A. B (2000) Archaeology, science-based archaeology and the Mediterranean Bronze Age metals trade. *European Journal of Archaeology*, 3 (1), 31-56.

Lefferts, K. C et al., (1981) Technical examination of the classical bronze horse from the Metropolitan museum of Art. *J. Amer. Inst. for Conservation*, 21, 1, 1-42.

Liritzis I (1980 a) Th-230/U-234 dating of speleothems in Petralona. *Anthropos 7*, 215-241 (Greek Anthropological Society, Athens).

Liritzis I (1980 b) Some Th-230/U-234 dates on detrital travertines from Petralona cave, Greece. *Revue d' Archaeometrie*, Sp. Issue, 111-120.

Liritzis. I and Galloway, R.B (1982a) The Th-230/U-234 disequilibrium dating of cave travertines. *Nucl. Instr. Methods*, 201, 507-510.

Liritzis. I and Galloway.R.B (1982b) A comparison of two techniques for the determination of the β-dose rate in ceramics for thermoluminescence dating. *Nucl. Instr. Methods*, 192, 555-558.

Liritzis, I (1983a) U-234/Th-230 dating contribution to the resolution of Petralona controversy. *Nature*, 299, 280-281.

Liritzis,I (1983b) New dating technique of ancient metals: Ra-226 method. Proceedings of 3rd Hellenic Conference in Physics, publ. by the *Panhellenic Union of Physicists,* Athens, 225-226 (in Greek)

Liritzis. I and Liritzis. B (1986) Dating of slags by TL and its archaeological implications. In Papastamataki A, (ed.), *The Slags of Ancient Hellenic Metallurgy*, Proceedings of a Seminar, *IGME*, Athens, 69-80.

Liritzis,I (1989a) U-series dating of speleothems relevant to cave art. *PACT* 17, II.2.4, 307-322.

Liritzis.Y (1989b) Dating of calcites : some aspects of radiation survey in caves and dose-rates. *Annales Geologiques des Pays Helleniques*, 34 (1), 123-136

Liritzis,I and Kokkoris,M (1992) Revised dose-rate data for thermoluminescence/ ESR dating. *Nuclear Geophysics* 6, 3, 423-443.

Liritzis,I, Arfara,I and Sideris.C (2006) U and Th vatiation in ancient slags, metals and metal ores: contribution to dating of metals. *Medit. Archaeol. & Archaeum*, vol.6, No2, 97-102.

Liritzis,I, Arfara,I, Sideris.C and Basiakos.Y (2007) U-Th and XRF measurements in copper ores, ancient metals and slags (in preparation).

Lorenz, A(ed.) (1983) Proposed recommended list of heavy element radionuclide decay data. *INDC (NDS)-149/ NE, IAEA Nuclear Data Section*, Wagramerstrasse 5, A-1400 Vienna.

Maddin, R and Muhly,J.D (1974) Some notes on the copper trade in the ancient mid-east. *Journal of Metals*, 24-29.

Maddin, R (1987) The copper and tin ingots from the Kas shipwreck. In *Old World Archaeometallurgy*, Heidelberg, 99-105, Selbstverlag des Deutschen Bergbau Museums Bochum, 1989.

McGeehan,V (1983) The relationship between metalwork copper sources and the evidence for settlement in the Greek Late Neolithic and Early Bronze Age. *Oxford Journal of Archaeology*, vol. 2, No.2, 147-180.

McGeehan, V (1996) The role and development of metallurgy in the late Neolithic and Early Bronze Age of Greece. Paul Astroms forlag,. *Studies in Mediterranean Archaeology* 122, 417 p.

Michael,C.T and Zacharias, N (2000) A new technique for thick source alpha counting determination of U and Th. *Nucl. Instr. Meth.* A, 439, 167-177

Moorey, P.R.S (1994) *Ancient Mesopotamian materials and industries.* Oxford, Clarendon Press.

Muhly, J.D (1989) The copper ox-hide ingots and the Bronze Age metals trade. *Iraq*, 39, 73-82.

Notton,J.H.S (1974) Ancient Egyptian gold refining: a reproduction of early techniques. *Gold Bulletin*, 7 (2), 50.

Northover, J.P (1987) Properties and use of arsenic copper alloys. In *Old World Archaeometallurgy*, Heidelberg, 111-118, Selbstverlag des Deutschen Bergbau Museums Bochum 1989.

Papadimitriou, G, Vardavoulias, M, and Marini, R (1988) Metallurgical study of ancient slags coming from copper production in Pelasgia-Larisa Kremaste. In *Archaeometallurgia, Ricerche e prospettive, Proceedings of International Colloquium on Archaeometallurgy*, 207-226, CLUEB Bologna.

Piggot, V.C (1999) A heartland of metallurgy: Neolithic/Chalcolithic metallurgical origins on the Iranian plateau. In *The Beginnings of Metallurgy.* (A.Hauptmann et al., eds.) Der Anschnitt, Beiheft 9, Bochum, 107-120.

Prescott.J.R and Jensen.H.E (1980) Low-level thorium and uranium determination for thermoluminescent dating. *Atomic Energy*, 26-32.

Renfrew, C (1967) Cycladic metallurgy and the Aegean early Bronze Age. *Am. J. Archaeology*, 71, 1-20.

Reedy, C.L (1997) *Himalayan bronzes: technology, style and choices.* Univ. of Delaware Press, 341 p.

Seruya, A.I and Griffiths, D (1995) Ageing processes in gold-copper-silver alloys. In *Archaeological Sciences, Proceedings of a conference on thev application of scientific techniques to the study of archaeology*, (Sinclair.A, Slater,E and Gowlett J.A.J., eds.) Oxbow Monograph 64, 132-135.

Schwarcz.H.P and Latham.A.G (1989) Dirty calcites I: Uranium series dating of contaminated calcite using leachates alone. *Chemical Geology (Isotope Geoscience)* 80, 35-43

Schwarcz, H.P (1980) Absolute age determination of archaeological sites by Uranium series dating of travertines. *Archaeometry*, 22 (1), 3-24)

Sjostrand.H and Prescott.J.R (2002) Thick source alpha counting: the measurement of thorium. *Ancient TL*, vol.20, No.1, 7-10.

Tarbuck, E and Lutgens, E (1987) *An introduction to physical geology*, 2nd Edition, Merrill Publishing, 55-57.

Tylecotte, R.F (1970) Early metallurgy in the Near East. *Metals & Metallurgy*, 285-293.

Tylecotte, R.F (1976) The Early Bronze Age, 14-52, In *A History of Metallurgy*, The Metals Society London.

Tylecotte, R.F (1987) *The early history of metallurgy in Europe*. Longman.

Taylor,J.J, Watling, R.J, Shell, R.A, Ixer, R.J, Chapman, R.J, Warner, R.B and Cahill, M (1995) From gold ores to artifacts in the British Isles: a preliminary study of a new LA-ICP-MS analytical approach. In *Archaeological Sciences, Proceedings of a conference on thev application of scientific techniques to the study of archaeology*, (Sinclair.A, Slater,E and Gowlett, J.A.J. eds.) Oxbow Monograph 64, 144-154.

Endnote

1 Bulk compositions undergo phase separation given sufficient time. Therefore, those alloys that are single phase at ambient temperature equilibrium cannot be dated, but for two phase at equilibrium may be to a first approximation be designated recent or antique according to whether they are still single phase or whether they have undergone phase separation. In fact in a given alloy of a composition measure the extent of phase separation at a given temperature after increasing intervals of time, this also permits one to determine the rate constant for phase separation for a given composition at a given temperature, repeated series of measurements at different temperatures the rate constant is determined at each case, a lengthy experimental programme. Gold alloy samples of various compositions and ages can be analysed to determine the degree of phase separation present, so providing information on the rate of phase separation at ambient temperature. Once sufficient reference data have been gathered, gold alloys of unknown antiquity could be analysed for their elemental and phase composition to give a rough indication of their age. In this crude dating approach particular attention should be exercised to distinguish phase separation due to slow cooling conditions rather than due to long period of time at ambient temperature.

Similar arguments apply to the use of ordering processes for dating gold alloys. Atomic ordering is in effect another form of phase transformation, whereby a random array of gold-copper atoms become redistributed into various more orderly arrangements in space. The ordering process is restricted to alloys of low silver content. Again, as with phase separation, determination of equilibrium diagram for ordering at ambient temperatures is needed.